THE VALIDITY OF THE EQUATION $P = T\, dv/dT$ IN THERMO-ELECTRICITY

By Edwin H. Hall

Jefferson Physical Laboratory, Harvard University

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The equation $P = T\, dv/dT$, in which P stands for the Peltier effect and v for the Volta effect between any two metals, was first obtained, I believe, by Lord Kelvin, comparatively late in his life. He derived it from a course of argument involving the imagined performance of a certain isothermal cycle. It was derived later by O. W. Richardson through a series of steps including his theory of thermionic emission and the imagined performance of a reversible cycle taking electrons from a metal at one temperature and putting them back into the same metal at a different temperature.

When Kelvin came to test his formula by the experimental data available to him he found no support for it. In fact, it is said that "the experimental verification failed by a thousandfold."

During the last few years experiments made by various skillful investigators measuring dv/dT in high vacua have perhaps reduced the ratio of the two sides of the professed equation to fifty; but it still remains so large that it would be considered a complete refutation of the equation's pretensions, if it were not possible to find an escape from this conclusion by dwelling upon the great difficulty of the experimental investigation.

I have not, until recently, given much attention to this equation; but two or three months ago my colleague, Professor Bridgman, who has lately been studying thermo-electricity intensively, put into my hands for criticism a manuscript in which, going over with modifications of his own the Kelvin method and the Richardson method, he had in both cases reached their conclusion. Studying Bridgman's manuscript I am, on the contrary, strongly inclined to the opinion that in each method the proof fails. As Professor Bridgman is now too much occupied with government work to give adequate attention to the question at issue, he has given me permission to present this question here.

I cannot reproduce at length either of the arguments. I can only point out what I believe to be the weak link in each. In the first, which was suggested by that of Kelvin, Bridgman assumes that when, by an applied e.m.f., electricity is carried along a metallic path from metal A, constituting one plate of a condenser, to metal B, constituting the other plate, the only heat phenomenon, except the negligible resistance effect, is the production or absorption of heat at the junction of the two metals, the ordinary Peltier effect. This assumption, which is vital to the argument, I question.

Let n_e be the number of free electrons per unit volume of a metal and n_i

the number of positive ions, atoms lacking each an electron. Within the interior of a metal in electrical equilibrium we must have $n_e = n_i$. At the surface, if the metal has a static charge, we do not have such equality. Now, according to my view, the free electrons and the positive ions, which are the products of the ionization of the atoms, obey the mass-law, so that everywhere in a metal we have

$$n_e \times n_i = a, \textit{ constant.}$$

If this view is sound, when we take electrons from one plate of a condenser and convey them to the other plate, we thereby disturb the electrical equilibrium in each metal. If one metal loses, for example, q electrons, we cannot have mass-law equilibrium in this metal until sufficient new ionization occurs therein to make the total number of free electrons if this metal only $\frac{1}{2}\ q$ less, and the total number of positive ions $\frac{1}{2}\ q$ more, than at first. In the other metal the converse operation must take place, re-association occurring there until the number of free electrons is $\frac{1}{2}\ q$ more and the number of positive ions $\frac{1}{2}\ q$ less than before. These processes of ionization and of re-association would balance each other in heat production if the two plates of the condenser were of the same metal, but otherwise they do not. Of course, wherever in the metals the ionization and the re-association primarily occur the result will presently appear at the surface, since any excess or deficiency of electrons in the interior of a metal must correct itself at the expense of the surface. Practically, then, we may regard the ionization and the re-association as occurring at the surface only.

Bridgman says that the failure of the equation $P = T\ dv/dT$ to bear the experimental test led Kelvin "to infer the existence of reversible heating effects at the surface of a metal when a charge is added to or subtracted from the surface, just as he had previously inferred the existence of the Thomson heat." Bridgman has thought that this inference was not justified and that sufficiently careful experiments would verify the equation. I think, on the contrary, that Kelvin's inference was sound, that the ionization and re-association phenomena which I have indicated are precisely the reversible heating effects at the surface which he infers, but does not visualize, and that the equation in question will never be justified by experiment.

The other line of argument begins with a metal in equilibrium with a surrounding electron atmosphere contained within an enclosure otherwise vacuous. The following quotations are from the second chapter of Richardson's *Emission of Electricity From Hot Bodies:*

"In this steady state there will be a definite number n [of electrons] per unit volume, on the average, in the vacuous enclosure, and they will exert a definite pressure p. If the enclosure is provided with a cylindrical extension in which an insulating piston can move backwards and forwards, this pressure p can be made do work against an external force." "The relation between the pressure of these electrons and the temperature of the enclosure can be found

by an application of the second law of thermodynamics." "All we need is an expression for dS, the increment in the entropy caused by motion of the piston. If φ is the change in the energy of the system which accompanies the transference of each electron from the hot body to the surrounding enclosure, then

$$dS = \frac{1}{T}\,[d(n\ v\ \varphi) + pdv]," \text{ etc.}$$

In writing this equation, which is fundamental to his argument, Richardson treats the case of a metal emitting electrons precisely as one treats the case of a body of water giving off steam to push against a piston. That is, he treats the emission of electrons as a process strictly comparable with evaporation. But there is an important difference between the two processes. In evaporation the thing given off is of the same substance as that left behind. In the emission of electrons this is not true. Evaporation leaves the constitution of the remaining liquid unchanged. Emission of electrons continually changes the constitution of the emitting metal, unless other electrons are put into the body to make good the loss. When a body emits a certain mass m of electrons under the conditions described by Richardson, the system under discussion takes in something more than heat energy; it takes in *substance*, the mass m of electrons. There is no analogue to this in the process of evaporation, and it remains to be shown that the equation which I have quoted from Richardson, an equation that holds beyond question for the case of evaporation, holds also for the case of emission of electrons.

One cannot, according to my view, meet this difficulty by supposing the body of metal made very large, so large that the static charge produced on it by the emission of a mass m of electrons without compensation would be negligibly small. For, if the loss of the electrons is not made good, the mass-law, requiring that $n_e \times n_i$ shall remain constant within the metal, will cause ionization there proportional to m, without regard to the amount of the metal; and this ionization will introduce a consumption of heat for which Richardson has made, I think, no provision.

ON THE EQUATIONS OF THE RECTANGULAR INTERFEROMETER

BY CARL BARUS

DEPARTMENT OF PHYSICS, BROWN UNIVERSITY

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1. Auxiliary Mirror.—It is desirable to deduce the fundamental equations more rigorously than has heretofore[1] seemed necessary. Figure 1 is supplied for this purpose, and represents the more sensitive case, where in addition to the mirrors M,M', N,N' (all but M being necessarily half silvers), there is an